

Electronic properties of Polymers: a microscopic view

Michel Côté

*professeur, Département de physique et Groupe de recherche
en physique et technologie des couches minces (GCM),
Université de Montréal, C. P. 6128 Succursale Centre-ville,
Montréal (Québec) H3C 3J7, Canada**

Abstract

Polymers are currently being used extensively because of their structural properties (plastic!) and are more and more being sought for their electronic properties. Nowadays, blue light emitting diodes can readily be made with polymer materials, something very difficult to achieve with conventional inorganic semiconductors.

In this article, we will present several theoretical models to calculate the electronic properties of polymers starting from a simple model and finishing with results that use density functional theory calculations in order to form a microscopic view of the nature of the electronic wave functions of polymers. We will use poly(*p*-phenylene) to illustrate how these calculations are carried out and to explain some of the relaxations of the structure which are important when the polymer is excited.

*Electronic address: Michel.Cote@umontreal.ca; URL: <http://carbone.pmc.umontreal.ca/~michel/>

Introduction

What is a polymer? For certain, polymers are very big molecules (macromolecules), for others they are very small spaghetti. The answer depends on what characteristics one is considering. For an electronic structure physicist, a polymer can be considered as a one dimensional crystal and this is the view that will be adopted in this article. Obviously, the motivation for this view is because we are interested in particular properties of polymers, namely their electronic properties that can be use in electronic devices.

Not all polymers have "interesting" electronic properties. Polyethylene, see figure 1a, is the most common polymer with applications everywhere in our daily life, from plastic bags to bullet proof vests (hopefully not used in your everyday life!). Although polyethylene has exploitable structural properties, it does not have usable electronic properties. Polyacetylene, see figure 1b, was the first polymer to be made a conductor, an achievement that earned the 2000 Nobel prize of Chemistry for Heeger, MacDiarmid and Shirakawa[1]; it has attracted considerable interest because the electronic transport is via solitons[2]. But again, this polymer does not have interesting electronic properties for optical purposes since it does not luminesce. The next two polymers, poly(*p*-phenylene) depicted in figure 1c and poly(*p*-phenylenevinylene) in figure 1d , are among the most interesting because of their desirable optoelectronic properties.

Characteristics of Polymer Structures

Polymers come in different forms and atomic compositions but they all share a common feature: they are formed by repeating a unit which is made of a long chain of atoms, and for most polymers this chain is made of carbon atoms. Considering the polyethylene and polyacetylene in figure 1, what differentiates them is the bonding environment of the carbon atom, the former has a sp^3 configuration as in diamond whereas the latter has a $sp^2 - \pi$ bonding environment like in the graphite structure. Polymers which have carbon atoms in a sp^3 configuration are the ones we find in everyday applications such as plastic bags (polyethylene), clothing (polyesters) and styrofoam cups (polystyrene)[3]. Those polymers, which are presently considered for electronic applications, are generally of the second kind. The sp^2 bonding states constitute the atomic structure of the polymers whereas the unpaired

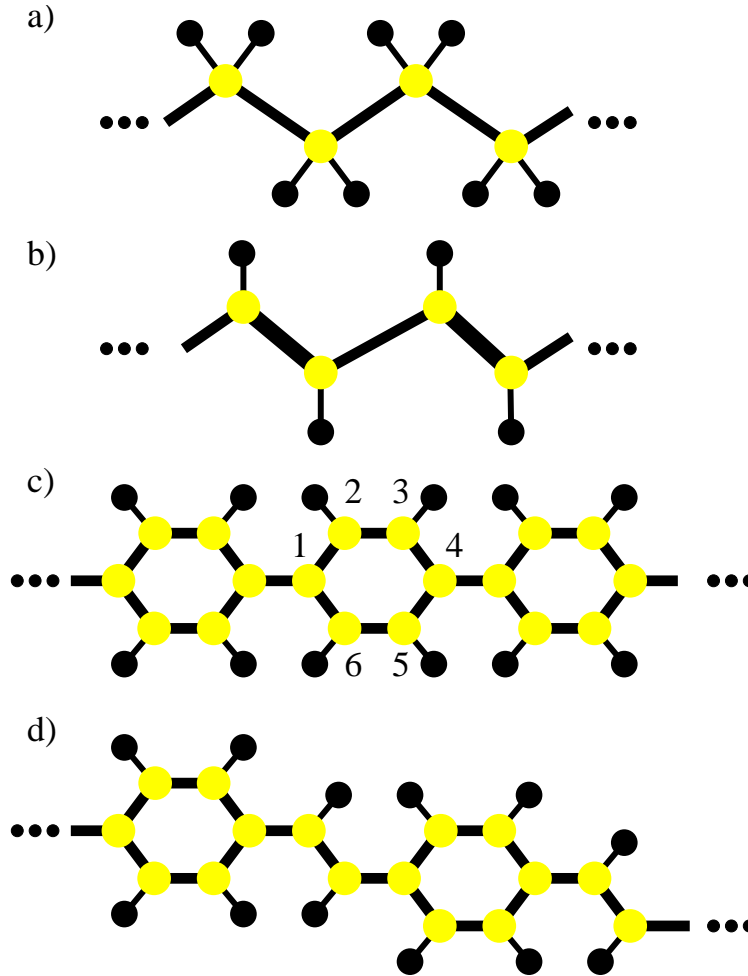


FIG. 1: Models of the polymers considered in this article: a) polyethylene, b) polyacetylene, c) poly(*p*-phenylene) and d) poly(*p*-phenylenevinylene).

π -electrons on each carbon atom form delocalized bonding states that are responsible for the optical and electronic properties of these polymers. For this reason, these polymers are not unrelated to graphite, fullerenes and carbon nanotubes.

A simple model...

The simplest model of the electronic properties of polymers considers only the unpaired π -electrons of the carbon atoms. Since these electrons are delocalized over the entire length of the chain, to a first approximation, they can be modelled by particles in a one dimensional

FIG. 2: Experimental absorption (right) and photoluminescence (left) spectra at 77 K of PPV oligomers containing from two to five rings from ref [4].

box. The energy levels for a particle in a box of length L are:

$$E_n = \frac{\hbar^2 \pi^2}{2m_e L^2} n^2. \quad (1)$$

The difference between two levels is:

$$\Delta E = \frac{\hbar^2 \pi^2}{2m_e L^2} [(n+1)^2 - n^2] = \frac{\hbar^2 \pi^2}{2m_e L^2} (2n+1). \quad (2)$$

Consider a polymer which is made of N repeated unit, each units is called a monomer. So, if this monomer has a length a , the total length of the polymer is $L = Na$. If we have m π -electrons on each monomer, the total number of π -electrons in this polymer is Nm ,

and since each energy level can accommodate two electrons (spin!), the number of occupied states is $Nm/2$. Hence, the energy gap of this polymer is:

$$E_g = \frac{\hbar^2 \pi^2}{2m_e (Na)^2} (2(Nm/2) + 1) = \frac{\hbar^2 \pi^2}{2m_e a^2} (m/N + 1/N^2) \sim \frac{1}{N}. \quad (3)$$

The last expression means that the energy gap is inversely proportional to the length of the polymer. Figure 2 shows the absorption spectra of oligomers of para(*p*-phenylenevynelyne) which I will refer to simply as PPV. Oligomers are molecules with a small number of repeated monomers, they are essentially very short polymers. From these spectra, we can clearly see the decrease of the optical gap as the oligomer becomes longer as predicted by the above simple argument. Note that this same argument is used to describe the size dependence of the band gap in quantum- well structures in conventional semiconductors. However, the above expression suggests that the optical gap goes to zero as the length of the polymer gets to infinity. Experimentally, this is not the case! The polymer PPV has an optical gap of about 2.5 eV and different polymers have different optical gaps. To account for this behaviour, we have to use of a more sophisticated model.

A step further ...

It is possible to do better than the particle in a box model of the previous section while keeping the model simple enough to gain physical intuition into the problem. The idea is to use a tight-binding model to represent the π -electrons in the polymer. To illustrate this method, we will consider the polymer poly(*p*-phenylene) (see figure 1c) which we will hereafter refer to simply as PPP. PPP can be viewed as benzene molecules fused together. The benzene molecule is a classic problem in tight-binding representing six carbon atoms on a ring. Using group theory arguments and the known symmetry group of the benzene molecule (D_{6h}), we have the possibility of singly or doubly degenerate states. In its simplest form, we can write the tight-binding model of the benzene molecule where the eigenstates have the form of a linear combination of π -orbitals: $\psi_n(r) = \sum_{i=1,6} c_n^i \phi_\pi^i(r)$ and the coefficients c_n^i need to be found. By considering only nearest neighbour interactions, an approach that is justified by using a sufficiently localised orbital, we can parameterize the matrix element $\langle \phi_\pi^i | H | \phi_\pi^j \rangle$: if $i = j$, this matrix element corresponds to orbitals on the same atom and refers to the on-site energy that we can arbitrary set to zero (this is just a rigid shift of

the spectrum); and if i and j are nearest neighbours the value of the matrix element is represented by λ . Since the benzene molecule has a total of 6 π -orbital which we identify in figure 1, we then have a 6×6 matrix which can be written as follows:

$$H = \begin{bmatrix} 0 & \lambda & 0 & 0 & 0 & \lambda \\ \lambda & 0 & \lambda & 0 & 0 & 0 \\ 0 & \lambda & 0 & \lambda & 0 & 0 \\ 0 & 0 & \lambda & 0 & \lambda & 0 \\ 0 & 0 & 0 & \lambda & 0 & \lambda \\ \lambda & 0 & 0 & 0 & \lambda & 0 \end{bmatrix} \quad (4)$$

Diagonalizing this matrix, we obtain the eigenvalues $\{-2\lambda, -\lambda, -\lambda, \lambda, \lambda, 2\lambda\}$. Because two electrons can occupy the same level, our 6 π -electrons are in the three lowest states. Note that the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) are both doublet states as is found experimentally for this molecule.

Now, in order to consider the polymer PPP, we have to modify our tight-binding model to account for the added bonds. Because the system is infinite, we have an infinite number of electronic states to consider but fortunately, we can exploit the translational symmetry of the system. As taught in elementary condensed-matter physics course, solutions for infinite periodic system are Bloch functions. Within the tight-binding model, we can write the Bloch function as $\psi_{kn}(r) = \sum_R e^{ikR} \sum_{i=1,6} c_{kn}^i \phi_{\pi}^i(r)$ where the sum over R goes over all unit cells (or monomers for the case of polymer) and k is the wave number of this Bloch function. The second sum is over the carbon atoms and we only have to solve for the coefficients c_{kn}^i . The beauty of the use of this symmetry is revealed when we consider the matrix element that we have to take into account. Because of the periodicity of the system, the only non zero matrix elements are those which involve wave functions with the same k vector and have the form $\sum_{R_i R_j} e^{ik(R_j - R_i)} \langle \phi_{\pi}^i | H | \phi_{\pi}^j \rangle$ where the first term gives an addition phase when the orbitals are not part of the same unit cell. We then have block diagonalized the full hamiltonian and our solution depends on the particular k -vector we are considering. However, because our unit cell has a finite length, any wave vector with a wavelength shorter than the length of the unit cell does not make sense, so the values that k can take are limited to be in the range $\{-\pi/a, \pi/a\}$, that is to say it is restricted to be within the first Brillouin zone. Working with polymers has a further advantage that they are a one dimensional system and therefore the Brillouin zone is a single line.

Coming back to the matrix hamiltonian for the PPP polymer, it has almost the same form as in the case of benzene. Since all the elements that we are considering for the case of benzene are within the same cell, no additional phase between these orbitals is needed. However, the carbon atoms labelled 1 and 4 are now bonded to three carbon atoms, two of which belongs to the same cell whereas the third belongs to a neighbouring cell. This additional interaction means that the hamiltonian now has components at the matrix positions 1:4 and 4:1 and that these matrix elements are multiplied by an additional phase factor. Taking the length of the cell to be a , these matrix elements are: $e^{ika}\langle\phi_{\pi}^i|H|\phi_{\pi}^j\rangle = e^{ika}\lambda'$ and its complex conjugate. We have chosen to parameterize this matrix element with λ' since we want to take into account the fact that it might be different than the others in the molecule, for example, the bond length might be different. The hamiltonian matrix of PPP is then:

$$H(k) = \begin{bmatrix} 0 & \lambda & 0 & e^{ika}\lambda' & 0 & \lambda \\ \lambda & 0 & \lambda & 0 & 0 & 0 \\ 0 & \lambda & 0 & \lambda & 0 & 0 \\ e^{-ika}\lambda' & 0 & \lambda & 0 & \lambda & 0 \\ 0 & 0 & 0 & \lambda & 0 & \lambda \\ \lambda & 0 & 0 & 0 & \lambda & 0 \end{bmatrix} \quad (5)$$

Solving this matrix and plotting the resultant energies as a function of the k vector, we obtain the electronic band structure. Figure 3 shows the band structure for PPP along with certain wave functions, the solid lines were obtained using a density functional theory method (more on this in the next section) whereas the dash lines are the results of the above tight-binding model[5]. Of course not all states are represented by the tight-binding model since we only considered the π -electrons, but we can clearly see that the states near the Fermi level are very well described by this simple model. Furthermore, it is obvious from the plots of the wave functions that the states near the Fermi level are indeed linear combination of π -orbitals on the carbon atoms.

A more elaborate model...

We have seen that simple models can go quite a long way to explain the electronic structure of polymers and are of great use in providing us with physical insight into the

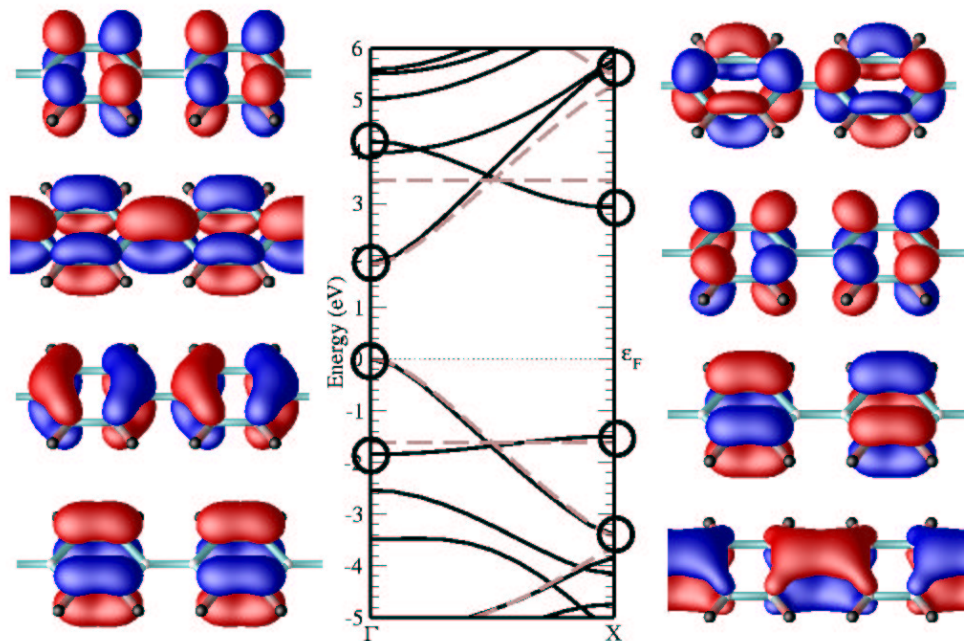


FIG. 3: Poly(*p*-phenylene) band structure. Solid lines are calculated using density functional theory and the dash lines are computed using the tight-binding model described in the text. The Fermi energy is at zero. A number of selected wave functions near the band gap are depicted; the corresponding states on the band structure are indicated by circles.

problem. However, we are often confronted with situations where the theory needs to provide accurate results which can be compared directly with experimental observations. A simple model like the tight-binding model above requires the fitting of some parameters (λ and λ') which means that we need to know something about the system we are studying. As the system becomes more involved (increasing numbers of atoms, different types of atoms, ...) the number of parameters to be fitted becomes too large to be practical. Fortunately, we have other methods that we can use to calculate the electronic properties.

Solving the electronic structure of a system is not a simple problem and in principle it means that we have to address the many-body Schrodinger equation for all the electrons of the system, a task which is impractical as soon as we are dealing with more than a few tens of electrons. However, over the years physicists have come up with intelligent methods to address this problem. One such method is based on the density functional theory (DFT). This method is what we call an *ab initio* method since it does not rely on any experimental parameter. Hohenberg and Kohn[6] proved in 1964 that only the electronic density of a

system is required to calculate its ground state properties and, the next year, Kohn and Sham[7] proposed a workable scheme. Essentially the idea of the method is to capture all the many-body effects into a functional which depends only of the density of the system. The problem and the challenge with the method are that, although we know that such a functional exists in principle, no one has an exact expression for it. Different working approximations have been found over the years and further development of appropriate functionals is the subject of much research activities.

Nevertheless, with the available functionals, we can calculate the electronic properties of many different systems which makes this method an ideal choice to study new materials such as the polymers under consideration in this article. This method has the further advantage that we can use it predict the properties of new compounds which do not as yet exist. Indeed, we used this feature of the method to predict the properties of boron nitride polymers[8] which are the III-V equivalent of usual carbon polymers.

Within the Kohn-Sham scheme, the basic equation to be solved is:

$$\left(\frac{-\hbar^2}{2m} \nabla^2 + V_{\text{ion}}(r) + V_H(r) + V_{xc}(r) \right) \psi_i(r) = \epsilon_i \psi_i(r), \quad (6)$$

where $V_{\text{ion}}(r)$ is the ionic potential created by the atoms of the system, $V_H(r)$ is the Hartree potential which can be calculated knowing the density and $V_{xc}(r)$ is the exchange and correlation potential obtained using some approximate functional. Therefore for a given density, we can write the hamiltonian and once we have solved it, we can determine the density by occupying the lowest eigenstates:

$$n(r) = \sum_{i=\text{occupied states}} \psi_i^*(r) \psi_i(r). \quad (7)$$

Since the density that we obtain has to be the same as the one used to formulate the hamiltonian in the first place, we need to iterate this procedure until the initial and the final densities converge to a common value, that is to say until the procedure becomes self-consistent. The eigenvalues that result from this method have been found to be a very good representation of the band structure of the system. A well known deficiency of these eigenvalues is the underestimate of the band gap but nevertheless we can often use the results to predict trends within a single family of compounds.

The results of such DFT calculations on the PPP polymer is also shown in figure 3. These calculations have no restriction on the orbital representation. Looking at the wave functions

near the Fermi level, we find that only π -orbitals are involved in these states. Eigenstates which involve sp^2 orbitals on the carbon atoms and s states on the hydrogen atoms are lower in energy. We should not be misled into thinking that the hydrogen atoms in PPP do not play any role in the electronic properties since they are not involved in states near the Fermi level. As we will see below, their role is more subtle.

Because the electronegativity of the hydrogen is less than that of carbon, there is a significant charge transfer ($\sim 0.3e$) from the hydrogen atom to the carbon ring. This means that the hydrogen is positively charged and the ring is negatively charged. The hydrogen atoms repulse each other but remain tightly bonded to their carbon atom. However, hydrogen atoms on different monomers could get further apart if the monomers rotate with respect to each other developing a torsion angle between the monomers located on the C—C bond between the monomers. The model in figure 1 shows a completely flat PPP structure (torsion angle of zero) but as far as the hydrogen atoms are concerned, they prefer to be at a maximum distance which implies a torsion angle of 90 degrees that minimizes the electrostatic energy of the system. Yet, the C—C bond between the monomers is not completely free to rotate. We have seen in the tight-binding model that π -electrons on each atom across that bond are interacting through a matrix element that we have parameterized by λ' . However, we have assumed that we were dealing with a completely flat structure such that the π -orbitals on adjacent monomer have maximum overlap. If there is a non-zero angle between the monomers, the axis of the π -orbitals will no longer be parallel. We can see that at a torsion angle of 90 degrees, there is no overlap between the π -orbitals and the matrix element is zero. We then have to explicitly include the torsion angle dependence into the matrix element. It is not hard to see that the dependence has the form $\lambda'(\theta) = \lambda' \cos(\theta)$.

The torsion angle dependence clearly affects the band structure of our system. Notably, if the angle is 90 degrees, the matrix elements are zero as mentioned above and the hamiltonian takes the form of the benzene hamiltonian. This means that the monomers are not communicating with each other and there is no energy gain by the delocalization of the π -electrons. To get maximum energy gain through delocalization, the desirable torsion angle is zero, a complete flat structure. The system is faced with a competitive effect between the electrostatic energy of the hydrogen atoms which prefer a torsion angle of 90 degrees and the energy gain from the delocalization of the π -electrons which favours a flat structure. With DFT calculations, we also determine the total energy of the system and we can there-

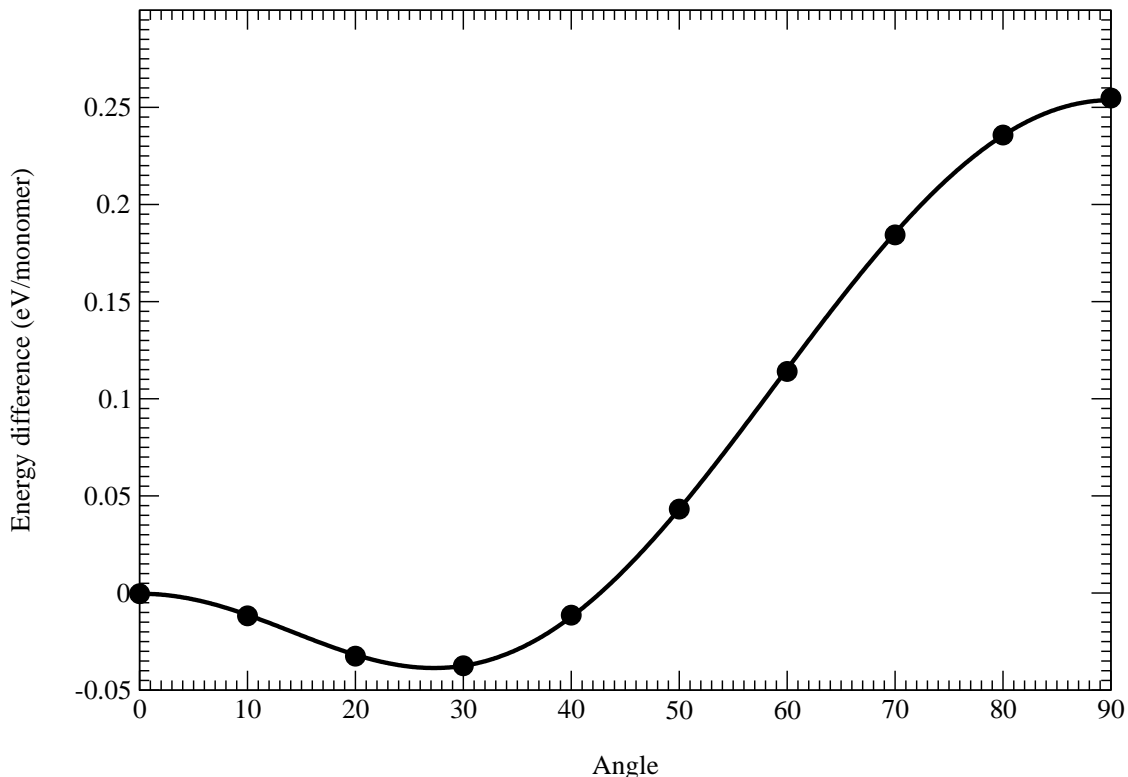


FIG. 4: Relative energy of poly(*p*-phenylene) as a function of the torsion angle between successive monomers

fore evaluate the stability of a structure with respect to a certain deformation. Since these calculations include all the effects discussed above, we then capture all the physics of the system. Figure 4 shows the relative energy of the PPP polymer with respect to the torsion angle and we can see that the predicted equilibrium torsion angle is around 25 degrees which compares well with available experimental values[9]. Note that the angle might change if we are considering polymers in solution where interactions between polymers are minimal or in thin films or in crystals where the interactions between polymers can affect this angle. Since the matrix element is related to this angle, the band gap of the system also depends on it. The smallest band gap is obtained for a completely flat structure and the largest for monomers at 90 degrees to each other. Replacing the hydrogen atoms by some other side chains would affect the torsion angle and hence the band gap.

The nature of the excited state in polymers

So far we have discussed only the ground state properties of the polymer but for many of the foreseen anticipated applications, the optical (excited states) properties are of greatest interest.

The band structure that we have calculated can be used to give an indication of the excited states. However, when we take an electron from the valence band and put it in the conduction band, there is an interaction between this electron and the hole that is left behind and if that interaction is strong enough, the electron binds to the hole resulting in the formation of an exciton. A important difference between conventional semiconductors and these polymers is the strength of the binding energy of the exciton which is usually of the order of a few meV for conventional semiconductors whereas in polymers, it can be as large as 1 eV[10]. Such large energies present *ab initio* methods with a great challenge since new methods have to be developed to take them into account.

Nevertheless, from what we have seen so far we can make several observations about the nature of the excited state. From figure 2, we see a large difference between the first peak of the absorption spectrum and the last peak of the photoluminescence spectrum. This difference is known as the Stokes' shift and is related to the fact that the atomic structure on which absorption is measured is not the same as the atomic structure of the observed photoluminescence. This means that the system has relaxed in the excited state and the energy levels no longer correspond to the ground state configuration.

One of the challenges is to identify the relaxation that takes place in the excited state. In figure 2, we see a series of peaks separated by about 0.2 eV. These peaks are associated with phonon replicas and this energy difference corresponds well to the stretching mode of the C—C bonds. However, we have also seen that the torsion angle affects the energy gap of the structure. An exciton wants to move to a region where the energy gap is minimum and possibly deform the structure to lower the gap. Since decreasing the torsion angle lowers the band gap, the exciton wants to flatten the polymer but that will cost too much elastic energy to do over the entire length of the polymer, so a compromise will have to be reached and only a certain length of the polymer will flatten. We can simulate this phenomenon using our tight-binding model of the previous section by considering a system where we have promoted one electron to the conduction band and let the system relax. Of course

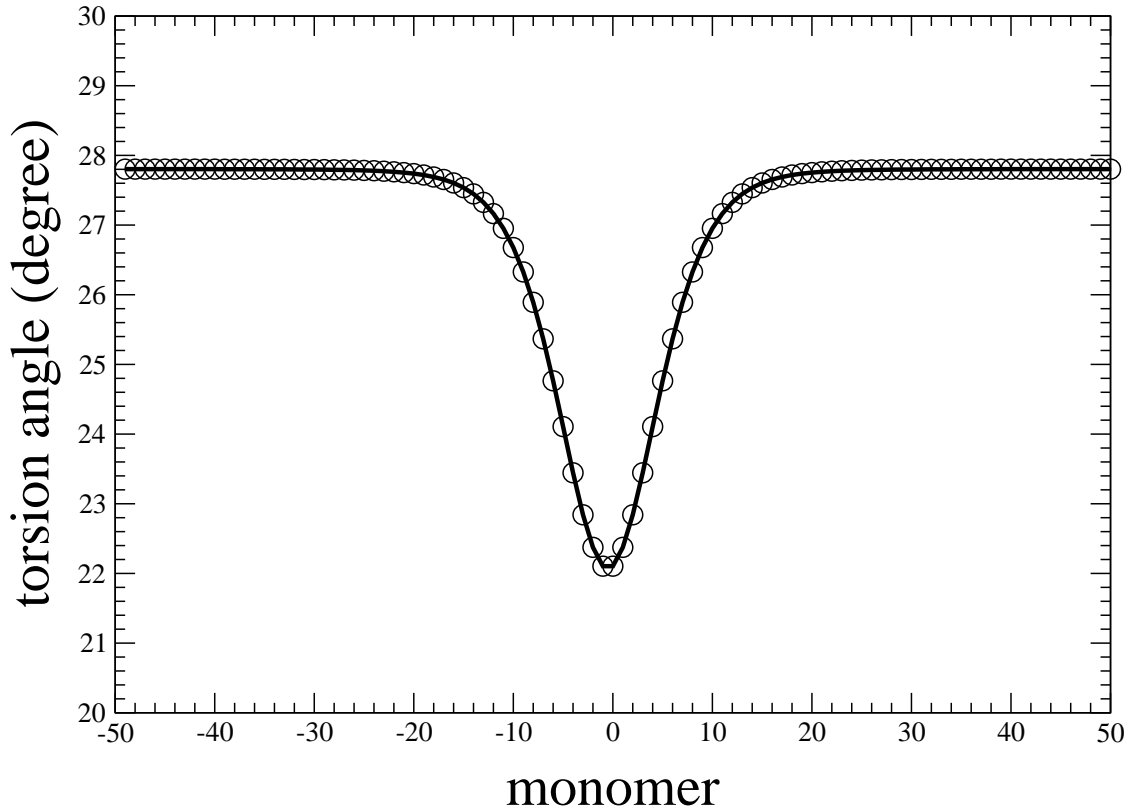


FIG. 5: Plot of the torsion angles between monomers showing the deformation due to the presence of an exciton. The extent of the deformation is about 20 monomers.

the only relaxation considered here is the torsion angle between monomers. The result is shown in figure 5. We can see a large deformation extending over 20 monomers which corresponds to a flattening of the polymer. The above discussion was concerned only with the relaxation of the torsion angle between monomers, however, the real relaxation that will actually take place through a combination of this torsional mode and the stretching mode of the polymer carbon backbone. We have also performed DFT calculations[11] which include all possible relaxations, a major computationally effort considering the size of the system involved. These calculations show that the deformation is not as extended as indicated by the tight-binding results of figure 5.

Conclusion

This article shows how we can use simple models to understand some of the electronic properties of polymers and how more sophisticated methods can give quantitative results in

good agreement with experimental values. We have also seen that the electronic properties of polymers are quite different than those of conventional semiconductors: the electron-hole interaction being a lot more important in polymers, it leads to strongly bonded excitons which can deform the structure. Although not addressed in this article, we can imagine that such coupling between the atomic structure and the electronic properties will greatly affect the transport properties in these systems.

Polymers and organic compounds offer numerous possibilities and new structural arrangements are constantly synthesized through chemical routes, an example being new polymers made with carbazole molecules[12]. A microscopic understanding of these new materials with the help of theoretical methods is essential in order to guide the design of polymers with desirable properties.

Acknowledgments

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- [1] <http://www.nobel.se/chemistry/laureates/2000/index.html>.
 - [2] A. J. Heeger, S. Kivelson, J. R. Schrieffer, and W.-P. Su, *Reviews of Modern Physics* **60**, 781 (1988).
 - [3] <http://www.psrc.usm.edu/macrog/index.htm>.
 - [4] J. Cornnil, D. Beljonne, C. M. Heller, I. H. Campbell, B. K. Laurich, D. L. Smith, D. D. C. Bradley, K. Mllen, and J. L. Brédas, *Chem. Phys. Lett.* **278**, 139 (1997).
 - [5] The tight-binding band structure was obtained with $\lambda = -2.53$ eV and $\lambda' = -2.8$ eV.
 - [6] P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964).
 - [7] W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).
 - [8] M. Côté, P. D. Haynes, and C. Molteni, *J. Phys.: Condens. Matter* **14**, 9997 (2002).
 - [9] C. Ambrosch-Draxl, J. A. Majewski, P. Vogl, and G. Leising, *Phys. Rev. B.* **51**, 9668 (1995).
 - [10] M. Rohlfing and S. G. Louie, *Phys. Rev. Lett.* **82**, 1959 (1999).

- [11] P. D. Haynes, M. Rohlfing, C. Molteni, E. Artachio, M. Côté, and R. J. Needs, unpublished.
- [12] J. F. Morin, S. Beaupré, M. Leclerc, I. Lévesque, and M. D'Iorio, *Appl. Phys. Lett.* **80**, 341 (2002).